

KEROSENE COMPOSITION

Field of the Invention

The present invention relates to kerosene compositions, particularly for use as heating fuels.

5 Background of the Invention

Kerosene is widely used for heating and for cooking purposes. Conventional kerosene, when used for heating purposes, has an oily smell when the kerosene is being handled on refueling and this is unpleasant for the user.
10 Furthermore, when used in open-type stoves, such as portable stoves and fan heaters, for example, or when used in a small kitchen range for cooking purposes, for example, the combustion is incomplete upon lighting and extinguishing and there is a disadvantage in that an
15 unpleasant smell is produced by the unburned hydrocarbons that are produced at this time.

On the other hand, the levels of safety and comfort (low production levels of NO_x, hydrocarbon compounds, CO, SO₂, etc. and no accompanying smell), for example,
20 demanded of oil stoves by the user, have also risen year by year. Furthermore, in recent years, problems have arisen with the emergence of kerosene that has been stored over the summer where with the use of such kerosene the oil stoves breakdown, and a demand for
25 improvement in the storage stability of kerosene has also arisen. In view of these circumstances, the kerosene that is to be used in oil stoves must satisfactorily fulfill such demands of the user.

A method in which a kerosene vaporising catalyst is
30 used, described in JP-B-59-16814, a method in which a deodorising agent is added to the kerosene, described in JP-B-54-32003, and kerosenes comprising n-paraffins and

iso-paraffins, described in JP-A-63-150380, for example, have been proposed for resolving the problems of the unpleasantness when handling and the unpleasant smell on ignition and on extinguishing, which are observed
5 generally with kerosenes.

However, with the method in which a kerosene vaporising catalyst is used, the catalyst deteriorates with the passage of time and so it has been difficult to maintain clean combustion over a prolonged period of
10 time. Furthermore, the method in which a deodorising agent is added to kerosene is not very effective because of the problem that the smell is not agreeable to some people. Furthermore, although kerosenes comprising n-paraffins and iso-paraffins do not have an unpleasant
15 smell when being handled and when being lit and extinguished and with which the exhaust gas is also clean, the production costs are greatly increased and there is therefore the problem that these kerosenes are expensive. Furthermore, kerosenes comprising
20 iso-paraffins and n-paraffins which have 9 or 10 carbon atoms as the main components have a lower density than existing kerosenes and the fuel consumption by volume is increased, and so, for example, it is likely that the JIS specification (of the Japanese Standards Association) for
25 fuel consumption in an oil stove will not be satisfied. Moreover, the flash point is reduced and there are also problems with safety.

Summary of the Invention

A kerosene composition is provided comprising at
30 least 99 wt% of a) at least one n-paraffins and/or iso-paraffins, said n-paraffins and/or iso-paraffins having from 7 to 18 carbon atoms and b) at least one cyclo-paraffins and/or alkyl derivatives thereof having from 9 to 18 carbon atoms.

Brief Description of the Drawings

Advantages of the present invention will become apparent to those skilled in the art with the benefit of the following detailed description of embodiments and
5 upon reference to the accompanying drawings.

Figure 1 is a graph of the change in the Saybolt value in an oxidation stability test for Examples 1 to 3 and comparative examples 1 and 2.

Figure 2 is a graph of the change in the amount of
10 peroxide in an oxidation stability test for Examples 1 to 3 and comparative examples 1 and 2.

Detailed Description of the Invention

The present invention provides kerosene compositions, particularly for use as heating fuels, which have
15 excellent performance. For example, they do not have an unpleasant odour when they are being handled, when they are being ignited or when they are being extinguished, the combustion exhaust gas is clean and the storage stability is high.

20 The present invention is intended to provide kerosene compositions for which the cost, fuel consumption and flash point are similar to those of kerosenes in general, and with which, unlike those obtained using conventional methods, the smell of the kerosene itself is very slight,
25 there is no unpleasant oily smell when it is being handled, with which there is no smell on ignition and extinguishing, which has good combustibility, with which the exhaust gas on combustion is clean, and which also has excellent storage stability.

30 It has been found that the aforementioned aims can be realised with kerosenes which contain specified amounts of n-paraffins and/or iso-paraffins, along with cyclo-paraffins and/or alkyl derivatives thereof, which all have specified numbers of carbon atoms, in place of the
35 conventional kerosenes obtained by the distillation of crude oil, and the present invention.

According to the present invention there is provided a kerosene composition containing at least 99 wt% of n-paraffins which have from 7 to 18 carbon atoms and/or iso-paraffins which have from 7 to 18 carbon atoms along with cyclo-paraffins, and alkyl derivatives thereof, which have from 9 to 18 carbon atoms. Preferably, at least 99 wt% of said n-paraffins and/or iso-paraffins have from 7 to 12 carbon atoms. Preferably, at least 99 wt% of said cyclo-paraffins have from 9 to 12 carbon atoms.

In said kerosene composition according to the present invention the ratio by weight of the n-paraffins and/or iso-paraffins to the cyclo-paraffins and/or alkyl derivatives thereof is preferably from 92:8 to 25:75, more preferably from 85:15 to 55:45.

Said kerosene composition according to the present invention preferably has a smoke point of at least 30 mm.

The n-paraffins and iso-paraffins which have from 7 to 18 carbon atoms which are used in the present invention can be obtained by taking synthetic gas obtained by partial oxidation, steam reforming from coal, natural gas, for example, and producing long-chain alkyl hydrocarbon polymer oil by means of a Fischer-Tropsch reaction and then carrying out hydrocracking and distillation. Furthermore, they can also be obtained in view of production costs by cracking or synthesis, for example, from the various fractions which are obtained in petroleum refining.

If the n-paraffins or iso-paraffins have less than 7 carbon atoms then the boiling point and flash point are too low and this is undesirable, and if the number of carbon atoms exceeds 18 then there are problems with low temperature fluidity, the boiling point is also raised too far and there is an adverse effect on the combustibility, which is undesirable.

Examples of the n-paraffins and iso-paraffins which can be used in the present invention include n-heptane, iso-heptane, n-octane, iso-octane, n-nonane, iso-nonane, n-decane, iso-decane, n-undecane, iso-undecane,
5 n-dodecane, iso-dodecane, 2-methylheptane, 2,2-dimethylhexane, 2-methyloctane, 2,2-dimethylheptane, 2-methylnonane, 2,2-dimethyloctane, 2-methyldecane, 2,2-dimethylnonane, and mixtures thereof.

The cyclo-paraffins, and the alkyl derivatives
10 thereof, which have from 9 to 18 carbon atoms and which can be used in the present invention can be obtained by the hydrogenation of the light oil and intermediate oil fractions obtained by the distillation of coal tar, or by
15 separation by distillation from crude oil and hydrogenation of the various distillate fractions.

If the number of carbon atoms of the cyclo-paraffins or alkyl derivatives thereof is less than 9 then the flash point is too low and this is undesirable, and if the number of carbon atoms exceeds 18 then the boiling
20 point is too high and there is an adverse effect on the combustibility, and this is undesirable.

Examples of the cyclo-paraffins and alkyl derivatives thereof which can be used in the present invention include n-butyl-cyclopentane, n-pentyl-cyclopentane, n-
25 hexyl-cyclopentane, isopropyl-cyclohexane, n-butyl-cyclohexane, n-pentyl-cyclohexane, n-hexyl-cyclohexane, cis-decahydronaphthalene, trans-decahydronaphthalene, 1-methyl-trans-decahydronaphthalene), 9-ethyl-(cis-decahydronaphthalene) and mixtures thereof.

30 The kerosenes of the present invention must contain at least 99 wt% of the aforementioned n-paraffins and/or iso-paraffins along with the cyclo-paraffins and alkyl derivatives thereof. If the content is less than 99 wt%, then aromatic components, olefinic components,
35 oxygen-containing components, nitrogen-containing components and sulfur-containing components are admixed

and a smell is observed when handling, igniting and extinguishing the kerosene, and the storage stability is of the same order as that of a general kerosene.

Furthermore, as indicated above, the mixing ratio by weight of the n-paraffins and/or iso-paraffins to the cyclo-paraffins and alkyl derivatives thereof is preferably from 92:8 to 25:75, and most preferably from 85:15 to 55:45. If the cyclo-paraffins and alkyl derivatives content thereof is high then the smoke point which indicates the combustibility is less than 30 mm and so this is undesirable, and if it is low then the flash point falls below the JIS specification and actual fuel consumptions (L/h) become greater than the indicated fuel consumptions by volume for the stoves and exceed the +10% of the JIS specification and so this is undesirable.

Preferably, said n-paraffins and/or iso-paraffins have been obtained by means of Fischer-Tropsch synthesis.

The kerosene compositions of the present invention comprising the compositions indicated above have the properties (1) to (4) indicated below, and in particular they have a high smoke point and excellent combustibility. As the smoke point is raised and the combustibility is improved, the time from ignition to complete combustion is shortened and complete combustion is promoted in the steady combustion state. Consequently there is no unpleasant smell or soot on ignition and the exhaust gas on ignition and during steady state combustion is also clean.

(1) Distillation IBP (Initial Boiling Point) is above 150°C, and preferably above 155°C, and the 95% distillation temperature is less than 270°C.

(2) Flash point is at least 40°C.

(3) Sulfur content is not more than 10 ppbm.

(4) Smoke point is at least 30 mm (compositions with smoke points of at least 35 mm, and even of 40 mm can also be obtained.)

Examples

5 The present invention will be illustrated by the following illustrative examples, which is provided for illustration only and is not to be construed as limiting the claimed invention in any way.

Example 1

10 An n-paraffin/iso-paraffin mixed oil of the composition shown in Table 1 was obtained by production with the SMDS (Shell Middle Distillate Synthesis) process, in which natural gas is partially oxidised, heavy paraffins are synthesised by means of
15 Fischer-Tropsch synthesis, and naphtha, kerosene and light oil fractions are obtained by hydrocracking of the heavy paraffin oil obtained, and distillation.

Table 1

Chemical Name	Concentration Wt%	Chemical Name	Concentration wt%
n-Heptane	0.01	n-Dodecane	0.73
iso-Heptane	0.07	iso-Dodecane	0.73
n-Octane	0.50	n-Tridecane	0.05
iso-Octane	5.66	iso-Tridecane	0.05
n-Nonane	26.95	n-Tetradecane	0.04
iso-Nonane	16.13	iso-Tetradecane	0.01
n-Decane	20.96	n-Pentadecane	0.02
iso-Decane	15.48	iso-Pentadecane	0.01
n-Undecane	3.83	n-Hexadecane	0.02
iso-Undecane	8.74	n-Heptadecane	0.01

20 Next, 92 parts by weight of the mixed oil and 8 parts by weight of decalin (decahydronaphthalene) were mixed together and an n-paraffin/iso-paraffin/decalin mixed kerosene was obtained.

Moreover, the concentrations of the iso-paraffins in
25 Table 1 indicate the concentrations of all of the branched hydrocarbons which have the same carbon number since it is difficult to determine the isomers with different structures. For example, iso-octane includes

all isomers such as 2-methylheptane, 2,2-dimethylhexane and the like.

Example 2

Seventy parts by weight of the
5 n-paraffin/iso-paraffin mixed oil obtained in Example 1
and 30 parts by weight of decalin were mixed and an
n-paraffin/iso-paraffin/decalin mixed kerosene was
obtained.

Example 3

10 Twenty five parts by weight of the
n-paraffin/iso-paraffin mixed oil obtained in Example 1
and 75 parts by weight of decalin were mixed and an
n-paraffin/iso-paraffin/decalin mixed kerosene was
obtained.

15 The properties of the kerosene mixtures of Examples 1
to 3 obtained in the way outlined above, kerosene of the
composition shown in Table 1 produced by the SMDS process
(Comparative Example 1) and JIS No.1 kerosene which is
generally sold (Comparative Example 2) are shown in Table
20 2.

Table 2

Property	Test Method	Example 1	Example 2	Example 3	Comp. Ex. 1	Comp. Ex. 2
Specific Gravity 15/4°C	JIS K 2249	0.761	0.794	0.882	0.735	0.800
Ignition Point °C	JIS K 2265	42	45	51	41	49
Sulphur Content (ppm)	JIS K 2545	>1	>1	>1	>1	42
Smoke Point (mm)	JIS K 2537	48	44	30	>50	24
Pour Point (°C)	JIS K 2269	> -30	> -30	> -30	> -30	> -30
Distillation °C	JIS K 2254	156.5	161.0	171.0	154.5	153.5
95%	JIS K 2254	199.0	197.0	192.5	199.5	265.0

As is clear from Table 2, the properties of the kerosene compositions of the present invention showed a smoke point much higher than that of Comparative Example 2, superior burning properties and a smaller sulphur fraction. Furthermore, they had a higher ignition point (flash point) than that of Comparative Example 1, and the JIS specification was satisfied.

The tests indicated below were carried out using the kerosenes of Examples 1 to 3 and Comparative Examples 1 and 2.

Stove Burning Test

Combustion performance tests were carried out using a wick top to bottom type stove and a petroleum fan heater. The fuel consumption for maximum burning and the CO/CO₂ ratio of the exhaust gas were measured in accordance with the test methods laid down in JIS S 2019 and JIS S 2031 in the case of the wick top to bottom type stove and in accordance with JIS S 2036 and JIS S 3031 in the case of the petroleum fan heater.

The results obtained are shown in Table 3.

Table 3

Burning Performance		Test Item	Example 1	Example 2	Example 3	Comp. Ex. 1	Comp. Ex. 2
Wick Top to Bottom Type Stove	Fuel Consumption	Measured L/h	0.294	0.278	0.246	0.299	0.251
		Difference Between Indicated and Measured (%)	+10.0	+4.2	-7.8	+12.0	-6.0
	CO/CO ₂ in Exhaust Gas		0.00004	0.00004	0.00006	0.00005	0.00037
	SO ₂ Content in Exhaust Gas	ppm	< 0.01	< 0.01	< 0.01	< 0.01	0.60
Fan Heater	Fuel Consumption	Measured L/h	0.367	0.352	0.315	0.374	0.348
		Difference Between Indicated and Measured (%)	+9.8	+3.6	-7.4	+12.0	+4.2
	CO/CO ₂ in Exhaust Gas		0.00030	0.00028	0.000028	0.00029	0.00032
	SO ₂ Content in Exhaust Gas	ppm	< 0.01	< 0.01	< 0.01	< 0.01	0.50

As is clear from Table 3, the kerosene compositions of the present invention had a lower CO/CO₂ and a much lower SO₂ content in the exhaust gas when compared with the kerosene of Comparative Example 2, and they provided a cleaner exhaust gas. Furthermore, the kerosene of Comparative Example 1 was such that the difference between the indicated and measured fuel consumption (L/h) per stove capacity did not satisfy the JIS specification of within $\pm 10\%$, while the kerosene compositions of the present invention did satisfy this JIS specification.

Odour Function Test

Twenty function tests were carried out using a wick top to bottom type stove and a petroleum fan heater, when ignited and when extinguished. The results are shown in Table 4.

Table 4

		Example 1	Example 2	Example 3	Comp. Ex. 1	Comp. Ex. 2
Odour of the Kerosene Itself		20	20	20	20	-
	Less than Comp. Ex. 2	0	0	0	0	-
	No Change	0	0	0	0	-
Wick Top to Bottom Stove	When Lit	20	20	20	20	-
	Less than Comp. Ex. 2	0	0	0	0	-
	No Change	0	0	0	0	-
Fan Heater	When Lit	18	18	16	18	-
	Less than Comp. Ex. 2	2	2	4	2	-
	No Change	0	0	0	0	-
When Extinguished	When Lit	20	20	20	20	-
	Less than Comp. Ex. 2	0	0	0	0	-
	No Change	0	0	0	0	-
When Extinguished	When Lit	19	19	17	19	-
	Less than Comp. Ex. 2	1	1	3	1	-
	No Change	0	0	0	0	-

As is clear from Table 4, the kerosene compositions of the present invention were such that the kerosenes themselves had less odour than the kerosene of

5 Comparative Example 2, and they also had less odour when they were lit and when they were extinguished.

Oxidation Stability Test

The Saybolt color and the amount of peroxide were determined as measures of the deterioration which had
10 occurred after a fixed period of time with carbon-arc irradiation at 40°C in a weathermeter (manufactured by the Suga Testing Machine Co.) as the test apparatus. The results are shown in Figures 1 and 2.

It is clear from Figures 1 and 2 that the kerosene
15 composition of the present invention was much less liable to deteriorate than the kerosene of Comparative Example 2 and had excellent storage stability.

By means of the present invention it is possible to provide a kerosene composition for which the cost, fuel
20 consumption and ignition point are the same as those of a general kerosene, with which the odour of the kerosene itself is very slight so that there is no unpleasant oily smell when it is being handled, which has good burning properties and provides a clean exhaust gas when it is
25 burned, and which has excellent storage properties, which has not been obtained with conventional methods.